MRL-R-1096

AR-005-193

DEPARTMENT OF DEFENCE

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION

MATERIALS RESEARCH LABORATORY

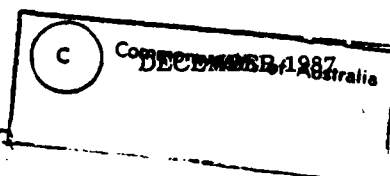### MELBOURNE, VICTORIA

REPORT

MRL-R-1096

AD-A192 704

EXAMINATION OF POLYSULFIDE SEALANTS BY
SCANNING ELECTRON MICROSCOPY

W. Mazurek and V.M. Silva

Approved for Public Release

DSTO
MELBOURNE

C Commonwealth of Australia

DECEMBER 1987

DEPARTMENT OF DEFENCE

MATERIALS RESEARCH LABORATORY

REPORT

MRL-R-1096

EXAMINATION OF POLYSULFIDE SEALANTS BY SCANNING ELECTRON MICROSCOPY

W. Mazurek and V.M. Silva

ABSTRACT

A procedure was developed for the examination of polysulfide sealants by scanning electron microscopy. This procedure was applied to manganese dioxide and dichromate-cured elastomers.

Calcium carbonate filler was identified in both types of sealants and the particle size was found to be < 4 μm. A technique was developed for the removal of the surface calcium carbonate exposing other solid additives. Amongst these, manganese dioxide was most obvious due to the large particle size and abundance. The presence of chromium containing particles could not be established and in practical terms it can be considered as a "solution" in the polysulfide. This implies a homogeneous phase reaction between the dichromate curing agent and the prepolymer and consequently a greater likelihood of a more complete curing of the polymer than that effected by manganese dioxide.

Approved for Public Release

CONTENTS

| Accession For	
NTIS GRA&I	☒
DTIC TAB	
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

QUALITY INSPECTED 4

EXAMINATION OF POLYSULFIDE SEALANTS
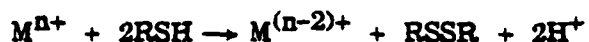
BY SCANNING ELECTRON MICROSCOPY

1. INTRODUCTION

Polysulfide sealants are used extensively in aircraft where there is a requirement for sealing metal joints and fasteners in integral fuel tanks, water tanks and canopies. The sealants used by the Royal Australian Air Force are formulated to conform to MIL-S-83430A [1] and MIL-S-8802E [2]. PR-1750 and PR-1422 are sealants manufactured by PRC (Products Research and Chemical Corporation, USA) and by Selley's Australia under licence from PRC, to meet the requirements of these specifications. One of the critical requirements is stability at elevated temperatures (>180°C).

The sealants are based on polysulfide polymers cured by the addition of a strong oxidizing agent. In the case of PR-1750, manganese dioxide is used as the curing agent whereas calcium dchromate is used in PR-1422. The former sealant has superior thermal stability compared with the dichromate cured system. The two factors most likely to affect the thermal stability of a given prepolymer, are the extent of cure and the thermal stability of the intermediates formed in the curing process. In most cases the curing agent does not form a homogeneous mixture with the prepolymer and therefore the extent of curing will be largely determined by its dispersion in the prepolymer. Manganese dioxide is usually added as a solid despersed in an inert medium whereas dichromates are added as a solution although it is not known whether they remain in solution after addition to the prepolymer. In order to appreciate the differences between these two common polysulfide curing agents it is essential to understand the chemistry of the curing process.

The curing (polymerization) process involves the oxidation of the terminal thiol groups in the polysulfide prepolymers to form the corresponding disulfide.

$$M^{n+} + H \{ SCH_2CH_2OCH_2OCH_2CH_2S \}_n S \rightarrow M^{(n-2)+} + [SCH_2CH_2OCH_2OCH_2CH_2S]_m$$

1
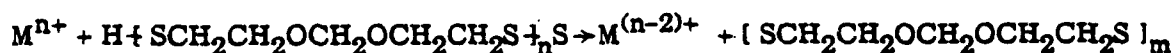
The process can be more simply expressed as:-

$$M^{n+} + 2RSH \rightarrow M^{(n-2)+} + RSSR + 2H^+$$

and it involves the net transfer of two electrons per molecule of disulfide. In some cases, in non-aqueous media, the process is known to occur via intermediate metal thiolate compounds. For example, with tellurium dioxide [3, 4] the following reaction occurs:

$$Te^{IV}O_2 + 4RSH \rightarrow Te^{IV}(SR)_4 + 2H_2O$$
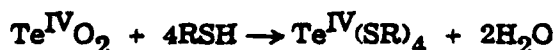
Oxidation of the thiolate then proceeds via intramolecular electron transfer. In the case of tellurium(IV) tetrathiolate, the process occurs in two steps. The first step is the formation of tellurium(II) dithiolate:

$$Te^{IV}(SR)_4 \rightarrow Te^{II}(SR)_2 + RSSR$$

The subsequent decomposition to tellurium(0) and the disulfide occurs less readily.

$$Te^{II}(SR)_2 \rightarrow Te^0 + RSSR$$
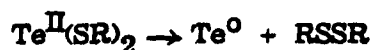
Although this reaction is carried out in a heterogeneous phase the tellurium thiolates dissolve in the reaction medium. Their decomposition ultimately results in the precipitation of tellurium.

Dichromate oxidation of thiols appears to proceed via a complex pathway. In aqueous media the following sequence of reactions [5] has been proposed:

$$Cr^{VI} + RSH \rightleftharpoons RSCr^{VI}$$

$$RSCr^{VI} + RSH \rightarrow Cr^{IV} + RSSR$$

$$RSCr^{VI} \rightarrow Cr^V + RS\cdot$$
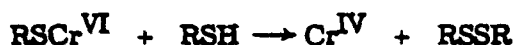
To date there have been no non-aqueous studies to indicate whether these reactions are applicable to the conditions encountered in polysulfide curing with dichromate. However this matter is presently being investigated by this Laboratory.

There has been a report of a dichromate-cured polysulfide sealant being extracted with EDTA solution and this has been used as evidence in support of the presence of chromium thiolate compounds in the cured sealant [6]. A large portion of the dichromate was found to be reduced to $Cr_2^{III}O_3$. The conclusions are justified providing that Cr_2O_3 was not solubilized by the extraction. Although the proposed sequence of reactions for the oxidation of thiols does not include the formation of Cr_2O_3, the formation of Cr(III) readily occurs at pH < 6 in aqueous media through a disproportionation reaction [7, 8].

2

$$3Cr(V) \longrightarrow 2Cr(VI) + Cr(III)$$

$$Cr(V) + Cr(IV) \rightleftharpoons Cr(VI) + Cr(III)$$

The possibility of Cr(III) thiolate compounds being present in the cured polysulfide [6] has not been explored in detail but air sensitive Cr(II) thiolates have been derived from simple thiols [9, 10].

Because of the high viscosity of the polysulfide prepolymers (15–1500 poise) and the heterogeneous phase oxidation by manganese dioxide particles, complete oxidation of the prepolymer can only occur with efficient mechanical mixing. However as the polymerization proceeds the viscosity of the mixture increases and contact between all reactants becomes less likely. Consequently the dispersion of the oxidant in the polysulfide is likely to be the dominant factor in determining the extent of the chemical reaction.

A possible mechanism for the oxidation of thiols by manganese dioxide has been suggested [11]. Manganese dioxide alone was found to be unreactive towards the oxidation of thiols. However, the activated oxide produced by alkali treatment of manganese dioxide, is known to form a coating of manganite ion on the manganese dioxide particles.

$$MnO_2 + 2OH^- \longrightarrow MnO_3^{2-} + H_2O$$
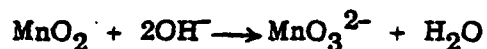
Although, in the presence of moisture, the blue colour of the manganite reverts back to the brown manganese dioxide, the product still retains its activity.
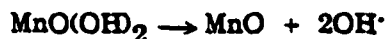
Thiol oxidation is thought to proceed through the coordination of the thiol to the manganese dioxide with the manganite ion providing a base for the deprotonation of the thiol.
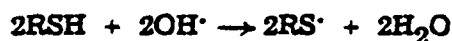

$$MnO_2 + 2RSH \longrightarrow$$

$$MnO + 2RS^\cdot \longrightarrow RSSR$$
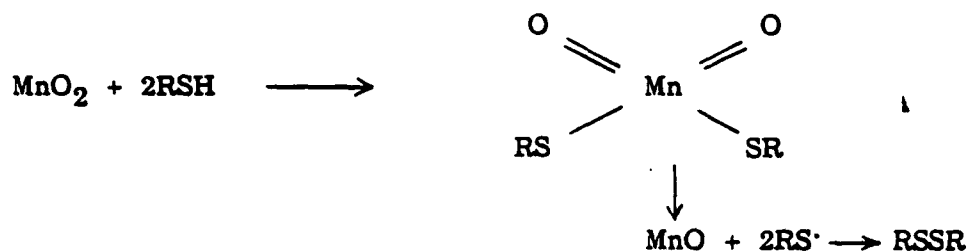
A hydrated manganese hydroxide has also been proposed [12];
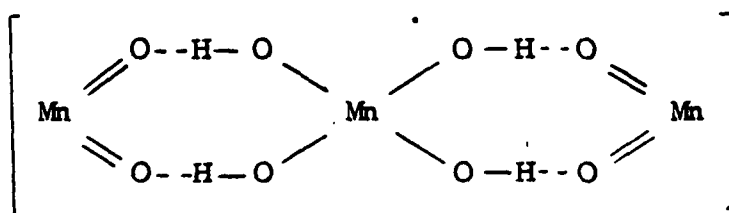
with the oxidation occurring via the generation of hydroxyl radicals.

$$MnO(OH)_2 \rightarrow MnO + 2OH\cdot$$

The thiol oxidation could then proceed as follows:

$$2RSH + 2OH\cdot \rightarrow 2RS\cdot + 2H_2O$$

$$2RS\cdot \rightarrow RSSR$$

On the other hand both electrochemical and chemical reduction of MnO_2 has been found to proceed to MnOOH [13] with little opportunity for direct formation of Mn(III) or Mn(II) thiolato compounds such as those formed by the reaction of Mn^{2+} salts with thiolates [14–16]. Thus the mechanism for the oxidation of thiols by manganese dioxide remains subject to speculation.

If the polysulfide curing process occurs via intramolecular electron transfer from the thiolate to the metal ion, the polymerization would then take place at the metal site. If the curing proceeds through the formation of a thiyl radical (RS.) then disulfide formation will occur mainly in the region where the radical concentration is highest. Assuming that one thiyl radical is generated by one metal ion and the oxidant is evenly dispersed in the polysulfide, polymerization will occur uniformly throughout the polymer. This situation could be applicable to manganese dioxide, however, it is difficult to envisage uniform dispersion of this insoluble solid on a molecular scale. In practice a 3 molar excess of manganese dioxide is used to ensure adequate curing indicating the difficulty of dispersing the oxidant in the polymer and in fact it is necessary to disperse the manganese dioxide in an inert medium prior to addition to the prepolymer.

In the case of dichromate, the reaction stoicheiometry is 6 moles of thiol to 1 mole of dichromate.

$$Cr_2{}^{VI}O_7{}^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$6\,RSH \rightarrow 3RSSR + 6H^+ + 6e^-$$
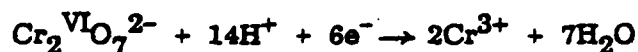
In practice a molar ratio of 5:1 is used indicating that the process proceeds stoicheiometrically and that there is intimate contact between the thiol and the dichromate in the reaction medium.

In this work both manganese dioxide (PR-1750 B1/2) and dichromate (PR-1422 B1/2) cured polysulfide sealants have been examined by scanning electron microscopy techniques so that a better understanding could be obtained about the interaction of curing agents within the sealant medium. Previous attempts to study this interaction by esr had proved unsuccessful [5].

4

2. EXPERIMENTAL

(a) Preparation of Elastomers

The polysulfide sealants PR-1422 B1/2 and PR-1750 B1/2 were cured by adding the curing paste to the base sealant in the ratio specified by the manufacturer Product Research Corporation, USA and Selleys Australia Pty Ltd, respectively. The components were mixed using a 25 mm diameter Teflon mandril rotating at approximately 150 rev. min^{-1}. After mixing, the sealants were cast into sheets approximately 3.5 mm thick. The sealants were prepared two years prior to examination.

Cured polysulfides without fillers were prepared by:

(a) curing Thiokol LP-2 prepolymer (120 g) with manganese dioxide Type C (Riedel-De Haen AG, Seelze-Hannoxer) (12.5 g) dispersed in Cerechlor (12.5 g)

(b) curing Thiokol LP-2 prepolymer (120 g) with ammonium dichromate (4.8 g) dissolved in a mixture of dimethylformamide (10 g) and water (2.4 g). These elastomers were heat aged for 7 days at $50^{\circ}C$ and prepared 4 months prior to examination.

(b) Scanning Electron Microscopy

The scanning electron microscope used was a Cambridge Stereoscan 5250 Mk2 with Link Systems Energy Dispersive X-ray Analysis 860 Mk 2.

All specimens were vacuum coated with a conducting film of carbon or gold prior to examination in the scanning electron microscope. Several imaging modes were used to elucidate the dispersion of the filler and curing agent in the elastomers, namely; secondary electrons for topographical information, back scattered electrons for atomic number contrast and energy dispersive x-ray mapping (x-ray emission) for specific element identification.

(c) Specimen Preparation and Examination

Several methods for producing fracture surfaces were used in order to obtain suitable surfaces for examination of the filler and curing agent in the elastomers. These were:

(i) freeze fracturing in liquid nitrogen,

(ii) room temperature fracturing,

(iii) cutting with a sharp blade,

(iv) part cut and part room temperature fracture (by hand).

5

The initial difficulty with specimen preparation was to find a method which not only revealed the filler material but also enabled its recognition in the scanning electron microscope (SEM) image. The lack of experience with the examination of this type of material under the SEM meant that a considerable effort was necessary in order to interpret the results.

Method (i) was not satisfactory as the fast brittle fracture did not reveal any recognisable filler particles. Methods (ii) and (iii) were used to establish that the sample preparation methods were not influencing the results as obtained from the SEM. The most satisfactory method of elastomer specimen preparation for the SEM turned out to be method (iv) where both cut and fractured sections could be examined on the one specimen. The observations made when using this method were reproducible.

3.   RESULTS AND DISCUSSION

(a) Identification of the Calcium Carbonate Filler

Examination of a cross section of PR-1422 B1/2 sealant sample under low magnification in the SEM, revealed a number of voids (< 0.5 mm diameter) caused by entrapped air during the preparation of the sealant (Figure 1). A closer examination of the specimen cross section produced by fracture, indicates a high filler density (Figures 2-4). The dominant filler in PR-1422 sealant is calcium carbonate (Table 1) and this requires identification prior to any assignments being made to the lesser components.

The obvious technique for separating the calcium carbonate from the remaining sealant components, is dissolution with mineral acid. It was found that immersion of the sealant specimen in 0.2 M HCl for 5 min produced a satisfactory result. Longer immersion times and higher acid concentrations resulted in polysulfide polymer degradation probably through acid hydrolysis of the methylenedioxy group.

Figure 1 shows the two halves of a sealant specimen cross section with one half having been exposed to acid treatment. At higher magnification the filler is more exposed in the fractured section (Figure 2) of the sealant rather than in the cut portion. A comparison of the acid treated and untreated specimens shows that the acid has removed most of the surface filler although there is evidence of some filler particles beneath the polymer surface.

When the filler in the sealant is compared with calcium carbonate (whiting) powder (Figure 3) the presence of a much smaller particle size is evident in the sealant. The maximum particle size encountered in the powder is approximately 40 μm whereas in the sealant the filler particles are no larger than 2 μm. It is not clear whether this is due to a finer grade of calcium carbonate incorporated into the sealant or whether the milling operations performed in the manufacture of the sealant had resulted in the disintegration of larger calcium carbonate particles. In order to resolve this problem the calcium carbonate powder was milled with Thiokol LP-2 prepolymer, on a triple roll mill, and the resultant mixture cured with dichromate. An examination of a fractured cross

section clearly shows the presence of large calcium carbonate particles in the elastomer (Figure 3(d-f)). This indicates that the calcium carbonate particles are not significantly effects by the milling process and that the grade of calcium carbonate used in PR-1422 B1/2 is of a smaller particle size than the Omyacarb 10 (Bathurst Australia) calcium carbonate shown in Figure 3.

Similar observations were made of the manganese dioxide cured PR-1750 B1/2 sealant (Figures 4 and 5) which also has a large calcium carbonate component as indicated by the analysis of a similarly formulated sealant (Table 2). In Figure 5a some small cracks are evident in the sealant which are probably due to the acid treatment as they are absent in the untreated specimen (Figure 5b).

(b) Distribution of the Oxidant

X-ray emission studies of the dichromate cured sealant PR-1422 B1/2, indicate a uniform distribution of chromium in the sealant to a depth of 0.8 μm (Figure 6). An examination of an ammonium dichromate cured polysulfide also shows the absence of chromium containing particles (Figure 7). Although the dichromate is added dissolved in dimethylformamide and water, it could be expected to precipitate in the non-polar prepolymer. The uniform distribution of chromium in the cured polymer implies that if precipitation does occur the particles are of a very small size, well dispersed and appear not to aggregate to any extent. This is consistent with the need of a near stoicheiometric quantity of dichromate for the curing of polysulfide prepolymers.

In order to obtain more accurate measurements of chromium dostribution, an x-ray emission scan was taken across the specimen cross section together with detector background levels (Figure 8a). None of the particles present in the specimen produced an emission corresponding to chromium. At high magnifications the electron back-scatter micrograph again failed to reveal any chromium containing particles greater than 0.1 μm (Figure 8) indicating the strong likelihood that chromium is present as a "solution" in the polymer.

The manganese dioxide-cured sealant, PR-1750 B1/2, after acid treatment, shows no obvious sign of filler particles (Figure 9a, b). The electron back-scatter micrograph however reveals a number of particles embedded in the surface (Figure 9c) but considerably fewer than the untreated specimen (Figure 9d). The x-ray emissions from the same area show that the majority of the large particles in the untreated specimen contain manganese (Figure 9f). This is supported by the evidence from the acid treated specimen (Figure 9e) where the correlation between the x-ray emissions and the particles in the electron back-scatter micrograph (Figure 9c) is more obvious. The largest manganese containing particle in the micrographs is approximately 20 μm. A micrograph of manganese dioxide itself shows that the particles can be as large as 30 μm (Figure 10). Electron back-scatter micrographs together with x-ray emissions leave no doubt that manganese containing compounds are present as discrete particles (Figure 11).

An examination of the fractured manganese dioxide-cured polysulfide polymer shows the presence of large particles of manganese dioxide at the apices of surface projections arising from the fracture (Figure 12). These are partly covered by the polymer whereas smaller particles that appear in the fracture plane are completely exposed. By comparison the ammonium dichromate cured polysulfide shows smaller surface projections (Figure 7a).

This situation in the manganese dioxide–cured polysulfide may arise because the energy required to propagate a fracture around a large particle is greater than that required for a small particle. The other possibility is that the polymer surrounding some of the manganese dioxide particles is more completely cured and consequently has a higher mechanical strength than the polymer some distance further. This implies that the manganese dioxide cured polysulfide is not homogeneously cured which is supported by the observation that the manganese dioxide–cured polysulfides are more likely to dissolve in dimethylformamide than chromate–cured polysulfides [18].

An attempt was made to ascertain the extent of the cure at various distances from the manganese dioxide particles by using a micro hardness tester on a 3 mm thick specimen of manganese dioxide–cured Thiokol LP-2 polysulfide embedded in epoxy resin. The surface of the polysulfide was polished to expose the manganese dioxide. However, no differences were found in the reactive forces to the applied load whether the load was applied at the manganese dioxide particle, next to it or further away. It was anticipated that a variation could be observed which was dependent on the distance from the manganese dioxide and this would have indicated localized curing. Unlike metals, to which micro hardness measurements are extensively applied, deformation of the substrate caused by micro hardness diamond stylus is not localized and bulk deformation is being observed. There is no other obvious technique which could be used to determine variations of the extent of polysulfide cure on a microscopic scale.

4.   CONCLUSIONS

Using the part cut and part fracture method for the examination of sealant specimens by scanning electron microscopy the following conclusions were reached.

The high filler content of the sealant is most obvious in a fractured cross section where calcium carbonate particles less than 2 μm in size were observed compared with < 40 μm for calcium carbonate powder. The absence of larger particles in the sealant was due to the compounding of the sealant but to a finer grade of calcium carbonate.

The calcium carbonate filler can be removed from the surface of the sealant specimen by treatment with dilute hydrochloric acid. In the case of the manganese dioxide–cured sealant, PR-1750 B1/2, the largest of the remaining particles were shown, by x-ray emission, to contain manganese (most likely manganese dioxide). Chromium containing particles could not be identified in the dichromate–cured sealant PR-1422 B1/2. It was concluded that the dichromate curing agent was very finely dispersed in the matrix and in practical terms could be regarded as a "solution".

Although the x-ray data does not reveal the oxidation state of chromium it is highly probable that most of it is in the reduced +3 state as solid Cr_2O_3. Whether the chromium was initially solubilized by reaction (as in the case of tellurium dioxide) with the prepolymer or whether the dichromate is naturally soluble in this medium is not clear. The practical consequences of this inference is that at some stage during the curing process a homogeneous reaction occurs between the dichromate and the

8

prepolymer. This has the potential of a homogeneous reaction which can lead to a complete cure.

The presence of discrete particles of manganese dioxide in the polysulfides indicates that the curing agent is not solubilized by reaction with prepolymer and that the curing reaction probably takes place at the surface of the manganese dioxide particles. Although this observation does not exclude the possibility of a manganese thiolate intermediate, it does tend to favour an indirect thiolate oxidation mechanism. This raises the question whether the extent of cure is the same in the immediate vicinity of the particle as it is some distance further away. An attempt was made to resolve this by the use of a micro hardness tester, but the lack of localized deformation in the elastomer failed to reveal any variations.

The generally poor thermal stability (120° - 180°C) in air of PR-1422, compared with PR-1750, is indicated by the weight losses [6, 19], and shear strength [20]. It is suggested that at these temperatures, the low thermal stability of PR-1422 is not due to the polymer but rather to the presence of chemical equilibria involving thermally unstable chromium-thiolate intermediates. The stability is also affected by the pH of the curing system [17]. The apparent absence of similar effects in PR-1750 supports the evidence for an indirect metal-thiol interactions and/or pH effects when manganese dioxide is used as a curing agent.

5. REFERENCES

1. ——— . (1982). Sealing Compound, Integral Fuel Tanks and Fuel Cell Cavities, Intermittent Use to 360°C. MIL-S-83430A.

2. ——— . (1984). Sealing Compound, Temperature-Resistant, Integral Fuel Tanks and Fuel Cell Cavities, High Adhesion. MIL-S-8802E.

3. Nakhdjavan, B and Klar, G. (1977). Liebigs. Ann. 1683.

4. Mazurek, W. (1986). Inorg. Chim. Acta, 113, 143.

5. Connett, P.H. and Wetterhaln, K.E. (1986). J. Am. Chem. Soc., 108 (8), 1842.

6. Knight, G.J. (———). Royal Aircraft Establishment Technical Memorandum Materials.

7. Mitewa, M., Bontchev, P.R. and Bojinov, V. (1972). Inorg. Nucl. Chem. Lett., 8, 51.

8. Krumpolc, M. and Rocek, J. (1985). Inorg. Chem., 24 (4), 617.

9. Dorfman, J.R., Rao, Ch. P. and Holm, R.H. (1985). Inorg. Chem., 24 (4), 453.

10. Mukherjee, R.N., Rao, Ch. P. and Holm, R.H. (1986). Inorg. Chem., 25 (17), 2979.

11. ——— . (1956). Internal Report, Thiokol Corp., USA.

12. Fatiadi, A.J. (1971). J. Chem. Soc. (B), 889.

13. Maskell, W.C., Shaw, J.E.A. and Tye, F.L. (1981). Electrochim. Acta, 26 (10), 1403.

14. Holah, D.G. and Coucouvanis, D. (1975). J. Am. Chem. Soc., 97 (23), 6917.

15. Costa, T., Dorfman, J.R., Hagen, K.S. and Holm, R.H. (1983). Inorg. Chem., 22 (26), 4091.

16. Seela, J.L., Folting, K., Wang, R-J., Huftman, J.C., Christou, G., Chang, H-R. and Hendrickson, D.N. (1985). Inorg. Chem., 24 (26), 4454.

17. Paul, D.B., Hanhela, P.J. and Haung, R.H.E. (1987). Proceedings of the International Symposium on Adhesives, Sealants and Coatings for Space and Harsh Environments, Meeting of Division of Polymer Materials, Science and Engineering, ACS Conference, Denver, April 1987. Plenum Press.

18. Mazurek, W. (1987). Unpublished results.

19. Hanhela, P.J. (1987). Private communication.

20. Ochittree, B.C. (1987). The Technical Cooperation Program, Subgroup P, Technical Panel 3 (Organic Materials), Minutes of the 33rd Meeting, U.S. Military Academy, West Point, NY and Army Materials Technology Laboratory, Watertown, MA, United States of America, p 151.

TABLE 1

Chemical Composition of Polysulfide Sealant PR-1422 B-2 [17]

Source[1]	Component	Percentage
Base Polymer	Filler	33
	($CaCO_3$)	(> 22)
	Water	0.6
	Toluene/MEK (1:1)	1.5
	Phenolic Resin	0.25
	Prepolymer	65
Cure Paste	Water	21
	Dimethylacetamide	30
	$CaCr_2O_7$	25
	Clay	22
	Carbon	1

[1] The base polymer and cure paste are used in the ratio 7.5:1 (w/w).

TABLE 2

Chemical Composition of Polysulfide Sealant PR–1422 B–2 [17]

Source[1]	Component	Percentage
Base Polymer	Filler ($CaCO_3$)	35
	Phenolic Resin	0.2
	Prepolymer	64
Cure Paste	MnO_2	47
	Carbon Black	12
	Sodium Stearate	4.6
	N,N'-diphenylguanidine	48

[1] The base polymer and cure paste are used in the ratio 10:1 (w/w).
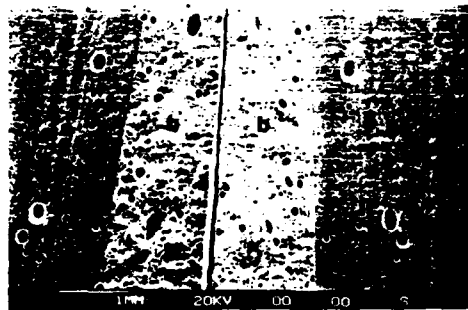
Figure 1. Two portions of PR-1422 B1/2 sealant, part cut (a) and part fractured (b). Hydrochloric acid treated portion is shown on the left, untreated portion on the right.
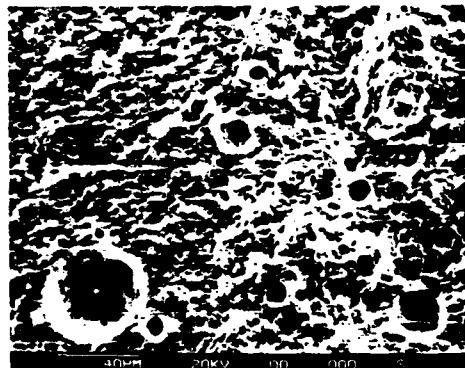
(a)
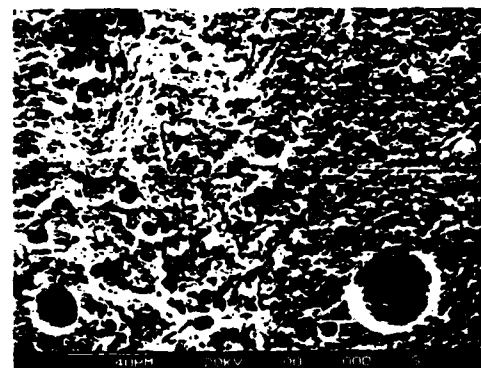
(b)
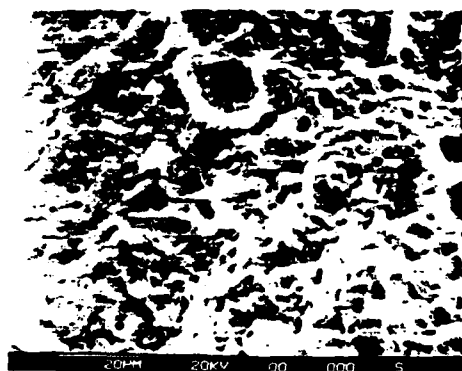
(c)
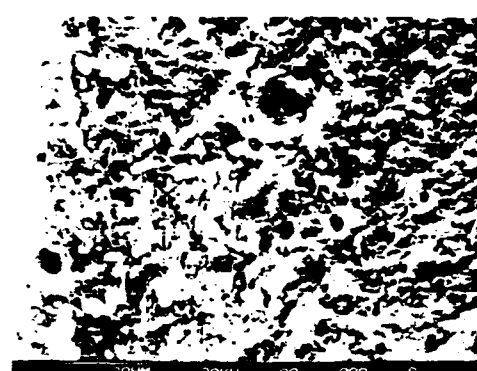
(d)

Figure 2.   Acid treated (a,c) and untreated (b,d) sections of PR-1422 B1/2 sealant at various magnifications.
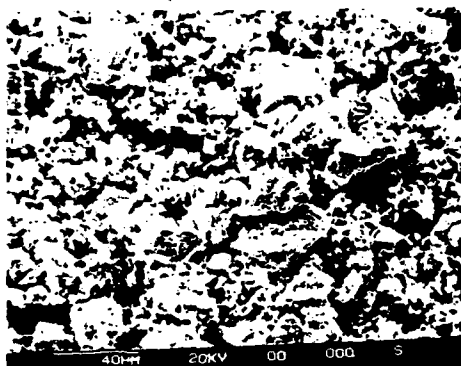
(a)

(b)
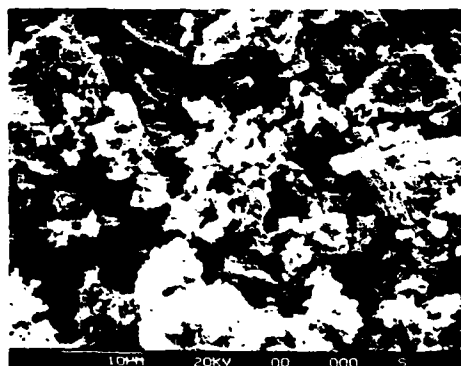
(c)

Figure 3. Calcium carbonate (whiting) powder.
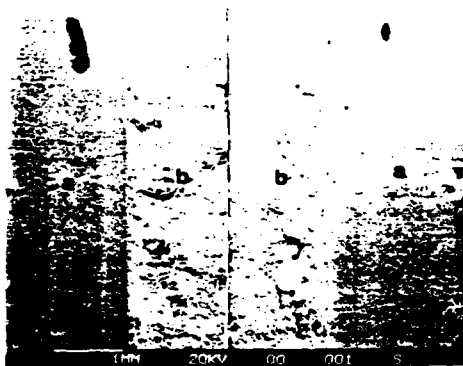
Figure 4. Two portions of PR-1750 B1/2 sealant, part cut (a) and part fractured (b). Hydrochloric acid treated portion is shown on the left, untreated portion on the right.
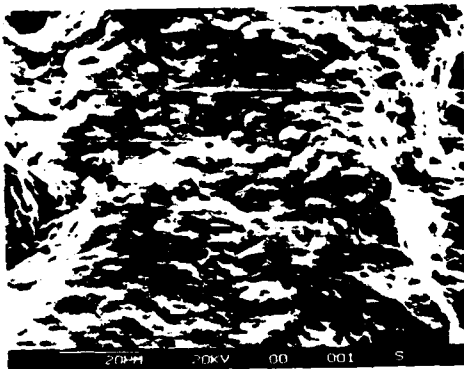
(a)
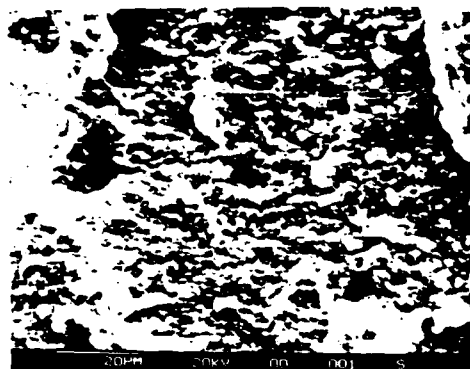
(b)
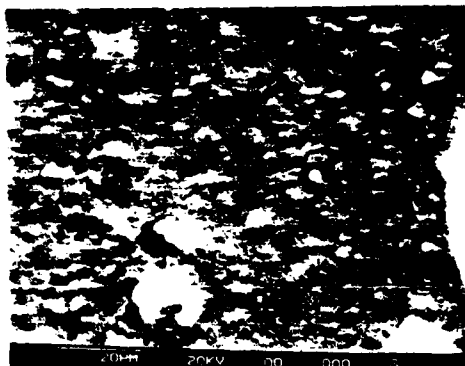
(c)
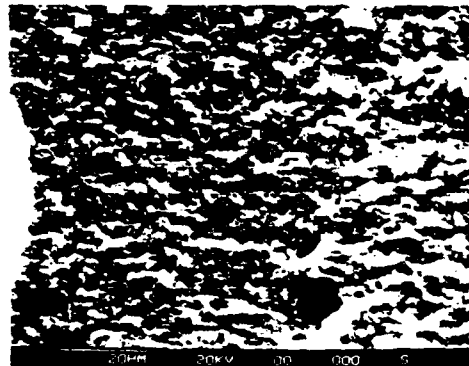
(d)

Figure 5. Acid treated (a,c) and untreated (b,d) sections of PR-1750 B1/2 sealant.
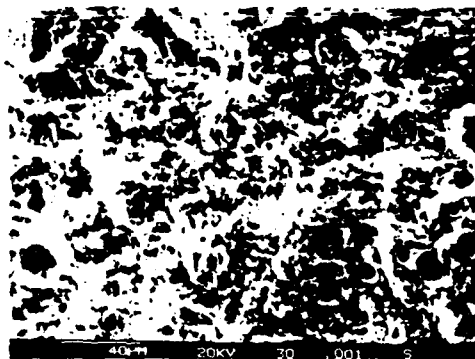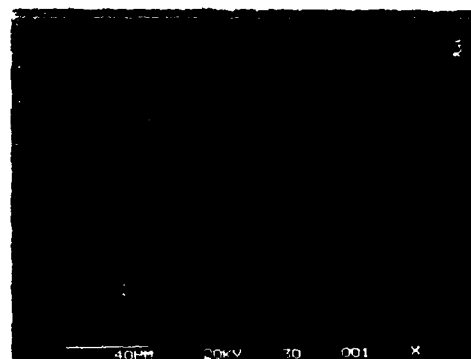
Figure 6. Secondary emissions (a) and x-ray (Cr) emissions (b) from the same area of PR-1422 B1/2 sealant section.
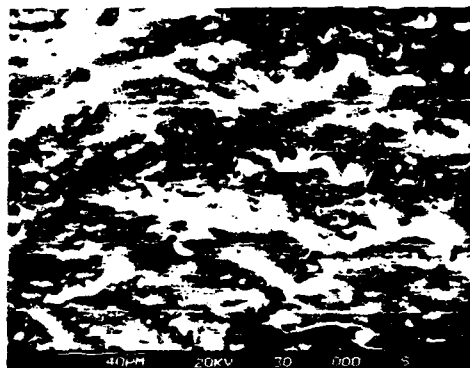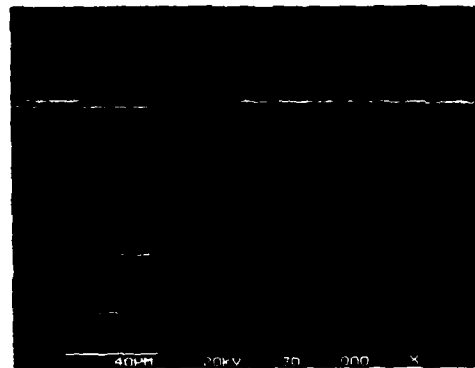
Figure 7. Secondary emissions (a) and x-ray emmissions (b) from the same area of an ammonium dichromate cured polysulfide.
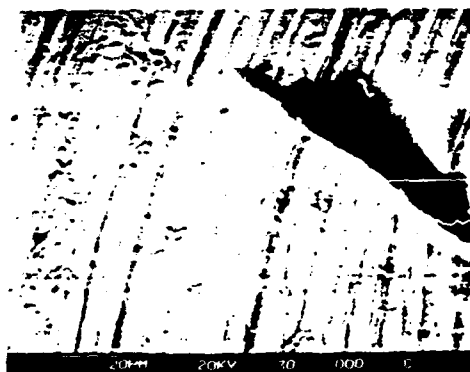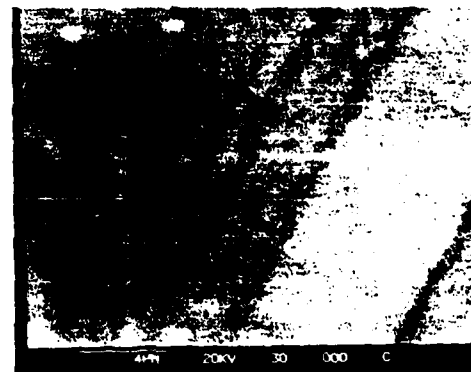
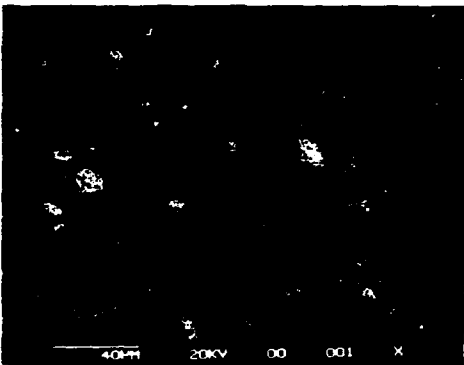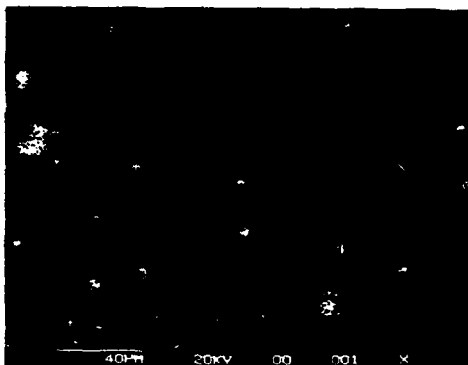**Figure 8.** Electron back scatter (a,b) with x-ray (Cr) emission signal superimposed (a) from
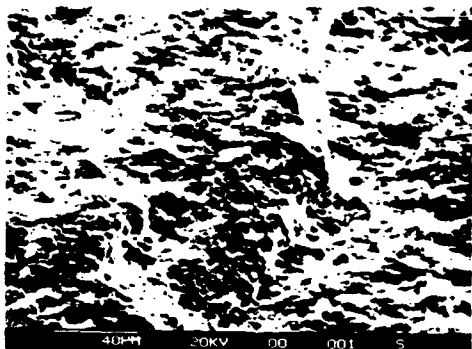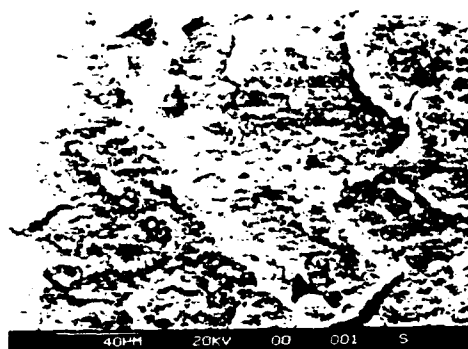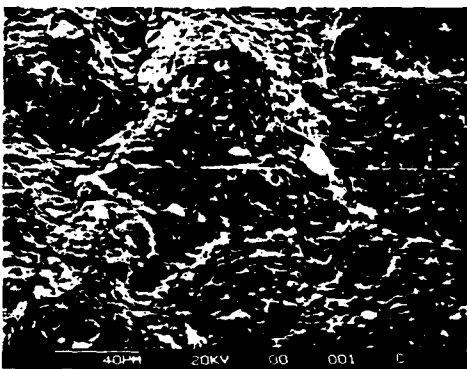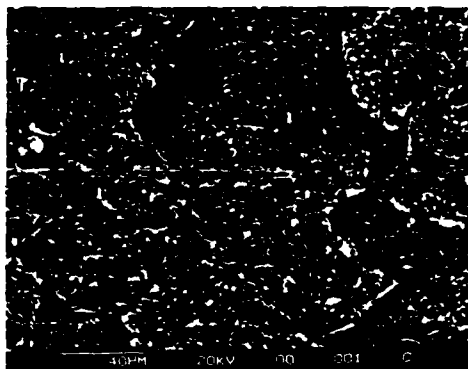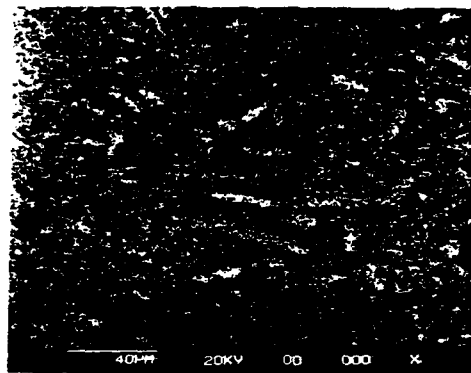
Figure 9. Secondary emissions from acid treated (a) and untreated (b) PR-1750 B1/2 sealant sections together with back scatter from the same area of acid treated (c) and untreated (d) sections and x-ray emissions from acid treated (e) and untreated (f) sections.
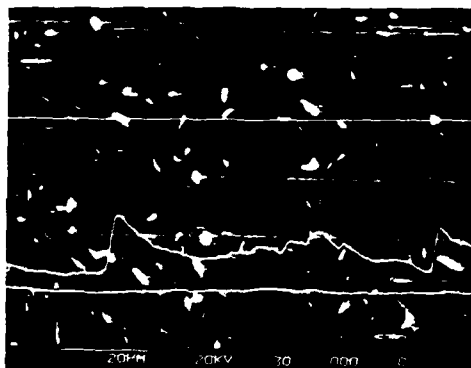
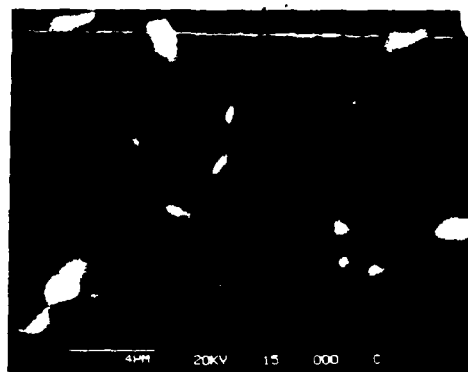(a)   (b)

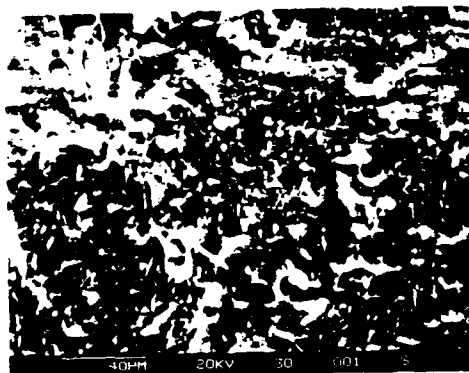Figure 10. Electron back scatter (a) and x-ray (Mn) emissions (b) from a manganese dioxide paste.
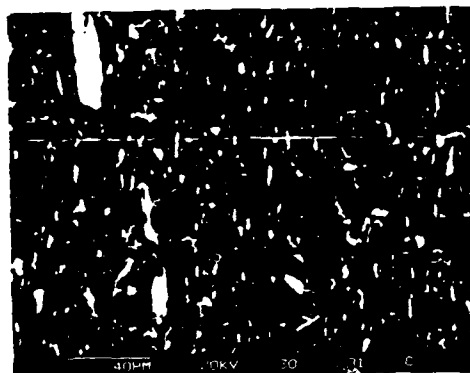

(a)   (b)
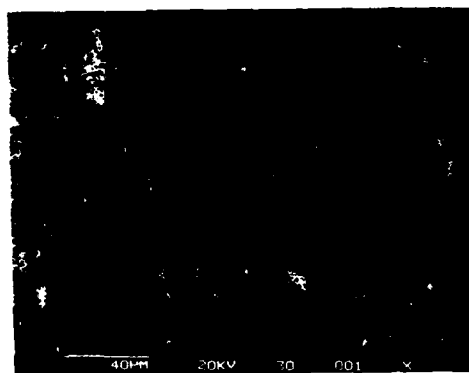
Figure 11. Electron back scatter (a,b) and x-ray (Mn) emission signal superimposed (a) - manganese dioxide cured polysulfide.

(a)

(b)

(c)

Figure 12. Secondary emissions (a) electron back scatter (b) and x-ray emissions (c) from a manganese dioxide cured polysulfide.

REPORT NO.	AR NO.	REPORT SECURITY CLASSIFICATION
MRL-R-1096	AR-005-193	Unclassified

TITLE

Examination of polysulfide sealants by
scanning electron microscopy

AUTHOR(S)	CORPORATE AUTHOR
W. Mazurek	Materials Research Laboratories
V.M. Silva	PO Box 50
	Ascot Vale, Victoria 3032

REPORT DATE	TASK NO.	SPONSOR
December 1987	DST 86/102	DSTO

FILE NO.	REFERENCES	PAGES
G6/4/8-3416	20	26

CLASSIFICATION/LIMITATION REVIEW DATE	CLASSIFICATION/RELEASE AUTHORITY
	Chief of Division,
	Protective Chemistry, MRL

SECONDARY DISTRIBUTION

Approved for Public Release

ANNOUNCEMENT

Announcement of this report is unlimited

KEYWORDS

Polysulfides	Sealants	Scanning electron microscopy

SUBJECT GROUPS   0071B

ABSTRACT

        A procedure was developed for the examination of polysulfide
sealants by scanning electron microscopy. This procedure was applied to
manganese dioxide and dichromate-cured elastomers.

        Calcium carbonate filler was identified in both types of sealants
and the particle size was found to be < 4 μm. A technique was developed for
the removal of the surface calcium carbonate exposing other solid additives.
Amongst these, manganese dioxide was most obvious due to the large particle
size and abundance. The presence of chromium containing particles could not
be established and in practical terms it can be considered as a "solution" in
the polysulfide. This implies a homogeneous phase reaction between the
dichromate curing agent and the prepolymer and consequently a greater
likelihood of a more complete curing of the polymer than that effected by
manganese dioxide.

SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED